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(54) Title: **HAIR BLEACHING AND COLOURING COMPOSITION WHICH COMPRISE TRANSITION METAL CATALYSTS**

(57) Abstract: A hair colouring composition comprising a first composition which comprises:(a) a transition metal salt or complex; which is first applied to the hair;and a second composition which comprises the following two compositions which are mixed just prior to application to the hair:(a) a composition comprising a water-soluble peroxygen oxidizing agent; and(b) a composition optionally comprising one or more oxidative hair colouring agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof.

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HAIR BLEACHING AND COLOURING COMPOSITION WHICH COMPRISE TRASITION METAL CATALYSTS

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BACKGROUND OF THE INVENTION

For hundreds of years, there has been a great interest in colouring human hair, and in particular in lightening the colour of human hair. In general, bleach compositions have
10 been used to lighten the colour of hair. Bleach compositions have comprised, for example, inorganic peroxygen oxidizing agents, which can be water soluble, and which can include hydrogen peroxide, inorganic alkali metal peroxides, such as sodium periodate, and inorganic perhydrate salts such as
15 metal salts of perborates. Moreover, these bleaching compositions have often included ammonia.

These compositions often failed to bleach hair efficiently—that is to say, these compositions have often
20 failed to provide for a large degree of hair lightening per amount of composition employed.

It is an object of the present invention to provide more efficient and effective hair bleaching compositions.
25

Thus it is an object of the present invention to provide improved hair colouring compositions.

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The following publications relate to the field of the invention:

U.S. Patent 6,004,355 discloses hair colouring compositions which comprise (a) a water-soluble peroxygen oxidizing agent, (b) an organic peroxyacid precursor oxidizing aid, and (c) one or more oxidative hair colouring agents. The compositions may be used in processes for colouring human or animal hair and may be conveniently provided in kits wherein each of the aforementioned components are individually packaged. This patent, at column 23, lines 20-35, discloses as ligands, a list which includes 1,4,7-trimethyl-1,4,7-triazacyclononane.

WO 97/24108 and WO 97/24107 disclose hair bleaching compositions comprising: a) a water - soluble peroxygen bleach and (b) a bleaching aid selected from organic peroxyacid bleach precursors and /or preformed organic peroxyacids. The products can provide hair bleaching and in-use efficacy benefits including reduced hair damage at lower pH.

U.S. Patent 5,873,910 discloses a process for the two-stage oxidation dyeing of keratin fibers by applying to the keratin fibers:

-in a first stage, at least one composition A containing at least one manganese salt and/or a manganese complex,

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-in a second stage, at least one composition B having a pH of greater than or equal to 6, and resulting from the extemporaneous mixing of at least one composition B1 containing at least one 4- substituted 1-naphthol and at least one composition B2 containing at least one oxidizing agent, and corresponding multi-compartment dyeing kit.

This patent discloses 1,4,7-trimethyl-1,4,7-triazacyclononane as a manganese complex to be used in its process at column 10, lines 20-25.

DE 19852972 discloses the use of 1,4,7-trimethyl-1,4,7-triazacyclononane in hair dye formation.

WO 99/33435 discloses the use of transitional metal complexes of a specified formula for dyeing keratin fibers. The transitional metals include manganese, iron, cobalt, ruthenium, molybdenum, and vanadium.

WO 01/28508 discloses a hair bleaching and colouring composition comprising a) an oxidising agent b) an oxidative and/or non-oxidative hair colouring agent; and c) ammonium carbonate and/or carbamate; wherein the pH of the composition lies in the range of from about 7 to about 9. The products can provide hair colouring, a wide variety of shades, grey coverage, reduced skin irritation and hair damage and reduced odour.

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SUMMARY OF THE INVENTION

The present invention is related to hair bleaching compositions suitable for the treatment of human or animal hair. According to one aspect of the present invention, there are provided two hair bleaching compositions which are used successively to bleach and/or lighten hair. The first composition comprises:

- 10 (a) a transition metal complex, which is applied first to the hair;

The second composition is next applied to the hair, and comprises the following compositions which are mixed just prior to application to the hair:

- 15 (a) a water-soluble peroxygen oxidizing agent;
and
 (b) optionally, one or more oxidative hair bleaching agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof.
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DETAILED DESCRIPTION OF THE INVENTION

As used herein, % means weight % of the total
5 composition unless otherwise designated. The compositions of
the invention are made using known ingredients or with
ingredients analogous to those known in the art. The
packages or containers to be used with the compositions of
the invention are made using known processes and materials
10 or by processes and materials which are analogous to those
known in the art.

Compositions of the invention are used in a two step
process for the bleaching and/or lightening of hair. That
15 is, a first composition comprising transition metal
catalysts is contacted with the hair, and then a second
composition comprises (a) a water-soluble peroxygen
oxidizing agent; and optionally (b) one or more oxidative
hair colouring agents. If the (b) one or more oxidative
20 hair colouring agents are present, then component (a) and
(b) are mixed just prior to application to the hair. After
mixture, this composition is then applied to hair. Then, a
period of time is allowed to elapse while the bleaching and
/o hair lightening reaction takes place and the hair is
25 then rinsed.

As used herein the term "hair" to be treated may be
"living" i.e. on a living body or may be "non-living" i.e. in
a wig, hairpiece or other aggregation of non-living fibres.
30 Mammalian, preferably human hair is preferred. However wool,
fur and other melanin containing fibres are suitable

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substrates for the compositions according to the present invention.

As used herein the term final bleaching composition
5 means the composition which is present in the hair after the transition metal composition and the bleaching composition have been added. The final hair bleaching compositions can contain, in addition to a mixture of active oxidizing agents, transition metal salts or complexes and oxidative
10 hair colouring agents such as, by way of example, an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof; and also may contain sequestrants, thickeners, buffers, carriers, surfactants, solvents, polymers non-oxidative dyes and conditioners.

15

As noted above, there is provided a hair bleaching composition comprising a first composition which comprises:

(a) a transition metal complex or salt;
20 which is first applied to the hair; and a second composition, which comprises the following two compositions which are mixed just prior to application to the hair:

25 (a) a water-soluble peroxygen oxidizing agent; and
(b) one or more oxidative hair bleaching agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof.

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The invention also relates to a composition comprising a transition metal wherein the transition metal salt and/or transition metal complex is selected from group 1B, 6B, 7B or 8B metals and an azamacrocyclic.

5

The invention also relates to a composition wherein a water-soluble peroxygen oxidizing agent is selected from hydrogen peroxide, sodium perborate, sodium percarbonate, and urea peroxide complexes.

10

The invention also relates to a composition wherein the transition metal complex is formed from a manganese salt and 1,4,7-trimethyl-1,4,7-triazacyclononane.

15

The invention also relates to a composition wherein said manganese complex is bis(octahydro-1,4,7-trimethyl-1H-1,4,7-triazinone-N1, N4, N7)-tri- μ -oxodimanganese bis hexafluorophosphate.

20

The invention also relates to a composition wherein the weight ratio of water-soluble peroxygen oxidizing agent to transition metal complex is in the range of from about 6000:1 to about 1:2; or about 4000:1 to about 100:1; or about 600:1 to about 60:1.

25

The invention also relates to a composition wherein the weight ratio of water-soluble peroxygen oxidizing agent to transition metal complex is from about 2000:1 to about 1:1;

30

The invention also relates to a composition wherein the weight ratio of water-soluble peroxygen oxidizing agent to

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transition metal complex is from about from 600:1 to about 60:1;

5 The invention also relates to a composition wherein the said transition metal salt and/or transition metal catalyst are present in a concentration ranging from about 0.0001% to about 0.2%, or from about 0.001% to about 0.5% or from about 0.001% to about 0.1% by weight of metal equivalents relative to the total weight of the final bleach
10 composition;

 The invention also relates to a composition, which further comprises a buffering agent;

15 The invention also relates to a composition having one or more oxidative hair bleaching agents as described above which has a pH of about 5 to about 11.

 The invention also relates to a composition as
20 described above which further comprises a surfactant selected from the group consisting of anionic, nonionic, cationic, zwitterionic, amphoteric surfactants and mixtures thereof.

25 The invention also relates to a hair bleaching kit comprising an individually packaged transition metal salt and/or transition metal complex with additional agents and individually packaged oxidizing or bleaching component with additional agents, which when mixed forms a composition of
30 the invention.

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According to a further aspect of the present invention, there is provided a hair bleaching composition comprising:

5 (a) from about 0.0001% to about 2% by weight of a transition metal and a second composition which comprises the following two compositions, which are mixed just prior to application to the hair:

10 (a) a composition comprising from about 0.01% to about 10% by weight of a water-soluble peroxygen oxidizing agent;

(b) optionally a composition comprising from about 0.0001% to about 7% by weight of one or more oxidative hair colouring agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof.

15

The invention also relates to compositions for bleaching human or animal hair wherein the hair bleaching composition comprises:

20

(a) a composition comprising from about 0.001% to about 1.0% by weight of a transition metal salt and/or transition metal complex;

25

which is first applied to the hair; and a second composition, which comprises the following two compositions which are mixed just prior to application to the hair:

30

- 10 -

- (a) a composition comprising from about 0.5% to about 20% by weight of a water-soluble peroxygen bleaching compound
- 5 (b) optionally, an oxidative hair colouring dye selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof.
- 10 (c) a composition comprising from about 5% to 50% additional agents selected from surfactants, buffering agents, oxidation bases and/or couplers from about 20% to about 95.5% by weight of an inert diluent

15 The invention also relates to a process for bleaching human or animal hair wherein the hair bleaching composition comprises applying to the hair the compositions described above.

20 It has been found that compositions of the present invention are unexpectedly effective for lightening and bleaching very dark brown or black hair.

For example, when (a) transition metal complex
25 composition of the present invention is first applied to very dark brown hair or black hair;

and then a second composition which comprises (a) a water-soluble peroxygen oxidizing agent; and (b) optionally
30 a composition comprising the following compositions (which are mixed just prior to application to the hair) are applied

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to said very dark hair brown or black hair there is obtained a very dramatic change colour of the hair.

The first composition comprising a transition metal
5 complex composition is applied first to the hair over the period of about a few seconds to about a minute. The second composition comprising an oxidizing or bleaching agent is applied and left on the hair for a period of about 10 minutes to about 45 minutes.

10

Change in hair colour and hair lightening can be measured by means which are known in the art. A customary scale for measuring the change in hair colour is described in terms of the variables: L, a, and b wherein L, a, and b
15 are described as follows: L indicates the lightness or darkness of the colour value. The higher the L, therefore, the lighter the hair, and the more fading that has occurred. When L is 0, the hair is black, and when L is 100, the hair is white. -a and +a represent changes in colour
20 tone from green to red. -b and +b represent the changes in colour tone from blue to yellow.

What follows now is a description of the ingredients which may be used in the compositions of the invention.

25

Transition metal complex or salt

The compositions of the invention comprise a transition
30 metal containing catalyst for the peroxide oxidizing agents. One suitable type of catalyst is a catalyst system

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comprising a heavy metal cation of defined catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no catalytic activity, such as zinc or aluminum cations, and a

5 sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S.

10 Patent No. 4,430,243 which is hereby incorporated by reference.

Other types of suitable catalysts include the manganese-based complexes disclosed in U.S. Patent No.

15 5,246,621 and U.S. Patent No. 5,244,594 which is hereby incorporated by reference .

Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$,

20 $\text{Mn}^{\text{III}}_2(\mu\text{-O})_1(\mu\text{-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\mu\text{-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\mu\text{-O})_1(\mu\text{-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in EP-A-0,549,272

25 which is hereby incorporated by reference. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

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For examples of suitable catalysts see U.S. Patent No. 4,246,612 and U.S. Patent No. 5,227,084 which is hereby incorporated by reference. See also U.S. Patent No. 5,194,416 which is hereby incorporated by reference which
5 teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(\text{OCH}_3)_3\text{-(PF}_6\text{)}$. Still another type of suitable catalyst, is disclosed in U.S. Pat. 5,114,606, which is hereby incorporated by reference. It is a water-soluble complex of manganese (III)
10 and/or (IV) with a ligand which is a noncarboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}\text{N}_4$ + and $[\text{Bipy}2\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}\text{bipy}2]\text{-(ClO}_4\text{)}_3$.

15

Further suitable catalysts are described, for example, in EP-A-0,408,131 (cobalt complex catalysts), EP-A-0,384,503, and EP-A-0,306,089 which is hereby incorporated by reference (metallo-porphyrin catalysts), and U.S.
20 4,728,455 all of which are hereby incorporated by reference.

Also suitable is (manganese multidentate ligand catalyst), U.S. Patent No. 4,711,748 and EP-A 0.224,952, (absorbed manganese on aluminosilicate catalyst), U.S.
25 Patent No. 4,601,845; (aluminosilicate support with manganese and zinc or magnesium salt), U.S. Patent No. 4,626,373 (manganese ligand catalyst), U.S. Patent No. 4,119,557 (ferric complex catalyst); DE-A-2,054,019 (cobalt chelant catalyst) CA-A-866,191 (transition metal
30 containing salts), U.S. Patent No. 4,430,243 (chelants with manganese cations and noncatalytic metal cations); and U.S.

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Patent No. 4,728,455 (manganese gluconate catalysts); all of which are hereby incorporated by reference.

Other types of suitable catalysts include the
5 manganese-based salts as described in U.S. Patent No. 5,873,610 which is hereby incorporated by reference.

The compositions of the invention comprise one or more transition metal catalysts. When compared against a
10 combination of all of the compositions of the invention after they have been mixed together (that is, the transition metal complex; the water-soluble peroxygen oxidizing agent composition; and the composition containing) the concentration of each catalyst is from about 0.0001% to
15 about 1% by weight and is preferably from about 0.001% to about 0.1% by weight.

The total combined level of catalysts in the compositions according to the present invention is from
20 about 0.0001% to about 2%, preferably from about 0.001 % to about 0.2%, more preferably from about 0.001% to about 0.1% by weight.

25 Water-soluble Peroxygen Oxidizing Agents

The compositions of the invention may comprise at least one water-soluble peroxygen oxidizing agent. Water-soluble as described herein means a peroxygen oxidizing agent
30 compound, which can be substantially solubilised in water.

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The peroxygen oxidizing agents useful herein are generally inorganic peroxygen materials capable of yielding hydrogen peroxide in an aqueous solution. Water-soluble peroxygen oxidizing compounds are well known in the art and
5 include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate and sodium peroxide and organic peroxides such as urea peroxide, melamine peroxide, and inorganic perhydrate salt oxidizing compounds, such as the alkali metal salts of perborates, percarbonates,
10 perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates, and the like. Mixtures of two or more such oxidizing agents can be used if desired. Preferred for use in the compositions according to the
15 present invention is hydrogen peroxide.

When compared against a combination of all of the compositions of the invention after they have been mixed together (that is, the transition metal complex; the water-
20 soluble peroxygen oxidizing agent composition; and the composition), the peroxygen oxidizing agent is present in the compositions of the present invention at a level of from about 0.01% to about 9%, preferably from about 0.1% to about 6%, more preferably from about 0.2% to about 4% by weight.

25

Applicant has also found that compositions of the present invention comprising particular oxidising agents with particular transition metal salts or catalysts with oxidative dyes are valuable for the delivery of good high
30 intensity colours with reduced levels of dye and peroxide. In particular applicant has now found that good hair

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colouring results can be achieved using the oxidizing systems of the present invention and up to about 84% less dye versus conventional hair colouring compositions. As such the compositions according to the present invention are
5 valuable for the delivery of good initial colour and wash fastness over time in addition to having low hair damage attributes.

10 Oxidative hair colouring agents

The compositions of the present invention may optionally include one or more oxidative hair colouring agents. Such oxidative hair colouring agents are used in
15 combination with the oxidizing systems of the present invention to formulate permanent, hair dye compositions.

Permanent hair dye compositions as described herein are compositions, which once applied to the hair are
20 substantially resistant to wash-out. Wash-out as described herein is the process by which hair colour is removed from the hair over time during normal hair cleansing regimen.

When compared against a combination of all of the
25 compositions of the invention after they have been mixed together (that is, the transition metal complex; the water-soluble peroxygen oxidizing agent composition; and the composition containing one or more oxidative hair colouring agents), the concentration of each oxidative hair colouring
30 agent is from about 0.0001% to about 7% by weight and is preferably from about 0.001% to about 2.0% by weight.

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When compared against a combination of all of the compositions of the invention after they have been mixed together (that is, the transition metal complex; the water-soluble peroxygen oxidizing agent composition; and the composition containing one or more oxidative hair colouring agents), the total combined level of oxidative hair colouring agents in the compositions according to the present invention is from about 0.01% to about 15%, preferably from about 0.01 % to about 10%, more preferably from about 0.1% to about 5% by weight.

Oxidative hair colouring agents which can be used in compositions of the invention can be selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof. Oxidative hair colouring agents which can also be called oxidative dyes are described in more detail below.

The dye forming intermediates used in oxidative dyes can be aromatic diamines, aminophenols and their derivatives. These dye-forming intermediates can be classified as; primary and secondary intermediates. Primary intermediates are chemical compounds, which by themselves will form a dye upon oxidation. The secondary intermediates, are also known as colour modifiers or couplers and are used with other intermediates for specific colour effects or to stabilise the colour.

The oxidation dye intermediates which are suitable for use in the compositions and processes herein include

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aromatic diamines, polyhydric phenols, aminophenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols).

Primary oxidation dye intermediates are generally colourless molecules prior to oxidation. The oxidation dye colour is generated when the primary intermediate is activated and subsequently joined with a secondary intermediate (coupling agent), which is also generally colourless, to form a coloured, conjugated molecule.

10

In general terms, oxidation hair dye precursors or intermediates include those monomeric materials which, on oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear coloured. For example, oxidation dye precursors capable of forming coloured polymers include materials such as aniline, which has a single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, and the like, ranging in colour from green to black.

Compounds such as p-phenylenediamine, which has two functional groups, are capable of oxidative polymerisation to yield higher molecular weight coloured materials having extended conjugated electron systems. Colour modifiers (couplers), such as those detailed hereinafter, are preferably used in conjunction with the oxidation dye precursors herein. A representative list of oxidation dye precursors suitable for use is found in Sagarin, "Cosmetic

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Science and Technology Interscience, Special Edn. Vol 2
pages 308 to 310, which is hereby incorporated by reference.

The typical aromatic diamines, polyhydric phenols,
5 aminophenols, and derivatives thereof, described above as
primary dye precursors can also have additional substituents
on the aromatic ring, e.g. halogen, aldehyde, carboxylic
acid, nitro, sulfonic acid and substituted and unsubstituted
hydrocarbon groups, as well as additional substituents on
10 the amino nitrogen and on the phenolic oxygen, e.g.
substituted and unsubstituted alkyl and aryl groups.

Nonlimiting examples of suitable aromatic diamines,
aminophenols, polyhydric phenols and derivatives thereof,
15 respectively, are the following compounds:

o-phenylenediamine,
m-phenylenediamine,
2-nitro-p-phenylenediamine,
20 1,3,5-triaminobenzene,
2-hydroxy-p-phenylenediamine,
2,4-diaminobenzoic acid,
sodium 2,4-diaminobenzoate,
calcium di-(2,4-aminobenzoate),
25 ammonium 2,4-diaminobenzoate,
trimethylammonium 2,4-diaminobenzoate,
tri-(2-hydroxyethyl)ammonium 2,4-diaminobenzoate,
2,4-diaminobenzaldehyde carbonate,
2,4-diaminobenzenesulfonic acid,
30 potassium 2,4-diaminobenzenesulfonate,
N,N-diisopropyl-p-phenylenediamine bicarbonate,

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- N,N-dimethyl-p-phenylenediamine,
N-ethyl-N'-(2-propenyl)-p-phenylenediamine,
N-phenyl-p-phenylenediamine,
N-phenyl-N-benzyl-p-phenylenediamine,
5 N-ethyl-N'-(3-ethylphenyl)-p-phenylenediamine,
2,4-toluenediamine,
2-ethyl-p-phenylenediamine,
2-(2-bromoethyl)-p-phenylenediamine,
2-phenyl-p-phenylenediamine laurate,
10 4-(2,5-diaminophenyl)benzaldehyde,
2-benzyl-p-phenylenediamine acetate,
2-(4-nitrobenzyl)-p-phenylenediamine,
2-(4-methylphenyl)-p-phenylenediamine,
2-(2,5-diaminophenyl)-5-methylbenzoic acid,
15 2-methoxy-p-phenylenediamine,
2,3-dimethyl-p-phenylenediamine,
2,5-dimethyl-p-phenylenediamine,
2-methyl-5-methoxy-p-phenylenediamine,
2,6-methyl-5-methoxy-p-phenylenediamine,
20 3-methyl-4-amino-N,N-diethylaniline,
N,N-bis-(2-hydroxyethyl)-p-phenylenediamine,
3-methyl-4-amino-N,N-bis-(2-hydroxyethyl)aniline,
3-chloro-4-amino-N,N-bis-(2-hydroxyethyl)aniline,
4-amino-N-ethyl-(piperidonoethyl)aniline,
25 3-methyl-4-amino-N-ethyl-□-(piperidonoethyl)aniline,
4-amino-N-ethyl-N-(morpholinoethyl)aniline,
4-amino-N-ethyl-N-(acetylaminooethyl)aniline,
4-amino-N-(methoxyethyl)aniline,
3-methyl-amino-N-ethyl-N-(2-acetylaminooethyl)aniline,
30 4-amino-N-ethyl-N-(mesylaminooethyl)aniline,
3-methyl-4-amino-N-ethyl-N-(□-mesylaminooethyl)aniline,

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- 4-amino-N-ethyl-N- (□-sulfoethyl) aniline,
3 -methyl-4-amino-N-ethyl-N- (□-sulfoethyl) aniline,
N- (4-aminophenyl) morpholine,
N- (4-aminophenyl) piperidine,
5 2,3-dimethyl-p-phenylenediamine,
2-isopropyl-p-phenylenediamine,
N,N-bis- (2-hydroxyethyl) -p-phenylenediamine sulfate,
o-aminophenol,
m-aminophenol,
10 p-aminophenol,
2-iodo-p-aminophenol,
2-nitro-p-aminophenol,
3,4-dihydroxyaniline,
3,4-diaminophenol,
15 2-hydroxy-4-aminobenzoic acid,
2-hydroxy-4-aminobenzaldehyde,
3-amino-4-hydroxybenzenesulfonic acid,
N,N-diisopropyl-p-aminophenol,
N-methyl-N- (1-propenyl) -aminophenol,
20 N-phenyl-N-benzyl-p-aminophenol sulfate,
N-methyl-N- (3-ethylphenyl) -p-aminophenol,
2-nitro-5 -ethyl-p-aminophenol,
2-nitro-5- (2-bromoethyl) -p-aminophenol,
 (2-hydroxy-5-aminophenyl) acetaldehyde,
25 2-methyl-p-aminophenol,
 (2-hydroxy-5-aminophenyl) acetic acid,
3- (2-hydroxy-5-aminophenyl) -1-propene,
3- (2-hydroxy-5-aminophenyl) -2-chloro-1-propene,
2-phenyl-p-aminophenol palmitate,
30 2- (4-nitrophenyl) -p-aminophenol,
2-benzyl-p-aminophenol,

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- 2-(4-chlorobenzyl-p-aminophenol perchlorate,
2-(4-methylphenyl)-p-aminophenol,
2-(2-amino-4-methylphenyl)-p-aminophenol,
p-methoxyaniline,
5 di-(2-aminoethyl-4-aminophenyl) ether,
di-(2-hydroxyethyl-4-aminophenyl) ether,
(4-aminophenoxy)acetaldehyde,
(4-aminophenoxy)acetic acid,
(4-aminophenoxy)methanesulfonic acid,
10 1-propenyl-4-aminophenyl ether isobutyrate,
di-(2-chloro-1-propenyl-4-aminophenyl) ether,
di-(2-nitro-1-propenyl-4-aminophenyl) ether,
di-(2-amino-propenyl-4-aminophenyl) ether,
di-(2-hydroxy-1-propenyl-4-aminophenyl) ether,
15 N-methyl-p-aminophenol,
3-methyl-4-aminophenol,
2-chloro-4-aminophenol,
3-chloro-4-aminophenol,
2,6-dimethyl-4-aminophenol,
20 3,5-dimethyl-4-aminophenol,
2,3-dimethyl-4-aminophenol,
2,5-dimethyl-4-aminophenol,
2-hydroxymethyl-4-aminophenol,
3-hydroxymethyl-4-aminophenol,
25 o-hydroxyphenol (catechol),
m-hydroxyphenol (resorcinol),
p-hydroxyphenol (hydroquinone),
4-methoxyphenol,
2-methoxyphenol,
30 4-(2-chloroethoxy)phenol,
4-(2-propenoxy)phenol,

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- 4- (3-chloro-2-propenoxy) phenol,
2-chloro-4-hydroxyphenol (2-chlorohydroquinone),
2-nitro-hydroxyphenol (2-nitrohydroquinone),
2-amino-4-hydroxyphenol,
5 1,2,3-trihydroxybenzene (pyrogallol),
2,4-dihydroxybenzaldehyde,
3,4-dihydroxybenzoic acid,
2,4-dihydroxybenzenesulfonic acid,
3-ethyl-4-hydroxyphenol,
10 3- (2-nitroethyl) -4-hydroxyphenol,
3- (2-propenyl) -4-hydroxyphenol,
3- (3-chloro-2-propenyl) -4-hydroxyphenol,
2-phenyl-4-hydroxyphenol,
2- (4-chlorophenyl) -4-hydroxyphenol,
15 2-benzyl-4-hydroxyphenol,
2- (2-nitrophenyl) -4-hydroxyphenol,
2- (2-methylphenyl) -4-hydroxyphenol,
2- (2-methyl-4-chlorophenyl) -4-hydroxyphenol,
2-methoxy-4- (1 -propenyl) phenol,
20 4-hydroxy-3 methoxycinnamic acid,
2,5-dimethoxyaniline,
2-methylresorcinol,
aniline,
p-chloroaniline,
25 p-fluoroaniline,
p-nitroaniline,
p-aminobenzaldehyde,
p-aminobenzoic acid,
sodium p-aminobenzoate,
30 lithium p-aminobenzoate,
calcium di- (p-aminobenzoate),

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ammonium p-aminobenzoate,
p-aminobenzenesulfonic acid,
potassium p-aminobenzenesulfonate,
N-methylaniline,
5 N-propyl-N-phenylaniline,
N-methyl-N-2-propenylaniline,
N-benzylaniline,
N-(2-ethylphenyl)aniline,
4-methylaniline,
10 4-(2-bromoethyl)aniline,
2-(2-nitroethyl)aniline,
4-aminophenylacetaldehyde,
4-aminophenylacetic acid,
4-(2-propenyl)aniline acetate,
15 4-(3-bromo-2-propenyl)aniline,
4-phenylaniline chloroacetate,
4-(3-chlorophenyl)aniline,
4-benzylaniline,
4-(4-iodobenzyl)aniline,
20 4-(3-ethylphenyl)aniline,
4-(2-chloro-ethylphenyl)aniline,
phenol,
p-chlorophenol,
p-nitrophenol,
25 p-hydroxybenzaldehyde,
p-hydroxybenzoic acid,
p-hydroxybenzenesulfonic acid,
ethylphenyl ether,
di-(2-chloroethylphenyl) ether,
30 di-(2-nitroethylphenyl) ether,
phenoxyacetaldehyde,

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phenoxyacetic acid,
3-phenoxy-1-propene,
3-phenoxy-2-nitro-1-propene,
3-phenoxy-2-bromo-1-propene,
5 4-propyphenol,
4-(3-bromopropyl)phenol,
2-(2-nitroethyl)phenol,
4-hydroxyphenylacetaldehyde,
4-hydroxyphenylacetic acid,
10 4-(2-propenyl)phenol,
4-phenylphenol
4-benzylphenol,
4-(3-fluoro-2-propenyl)phenol,
4-(4-chlorobenzyl)phenol,
15 4-(3-ethylphenyl)phenol
4-(2-chloro-3-ethylphenyl)phenol,
2,5-xlenol,
2,5-diaminopyridine,
2-hydroxy-5-aminopyridine,
20 2-amino-3-hydroxypyridine,
tetraaminopyrimidine,
1,2,4-trihydroxybenzene
1,2,4-trihydroxy-5-(C₁ - C₆-alkyl)benzene,
1,2,3-trihydroxybenzene,
25 4-aminoresorcinol,
1,2-dihydroxybenzene,
2-amino-1,4-dihydroxybenzene,
2-amino-4-methoxyphenol,
2,4-diaminophenol,
30 3-methoxy-1,2-dihydroxybenzene,
4,6-dimethoxy-3-amino-1-hydroxybenzene,

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2,6-dimethyl-4-(p-hydroxyphenyl)amino]phenol
and salts thereof.

Additional oxidation dye couplers suitable for use
5 herein include catechol species and in particular catechol
"dopa" species which includes dopa itself as well as
homologs, analogs and derivatives of DOPA. Other suitable
dye precursors are dihydroxyindole (DHI),
dihydroxyindolecarboxylic acid (DHICA) and derivatives
10 thereof, indolines and derivatives thereof. Examples of
suitable catechol species include cysteinyl dopa, alpha
alkyl dopa having 1 to 4, preferably 1 to 2 carbon atoms in
the alkyl group, epinephrine and dopa alkyl esters having 1
to 6, preferably 1 to 2 carbon atoms in the alkyl group.

15

The oxidation dye couplers (precursors) can be used
herein alone or in combination with other oxidation dye
couplers (precursors) mentioned above. The choice of a
single dye coupler (precursor) will be determined by the
20 colour, shade and intensity of colouration which is desired.
The following are preferred oxidation dye couplers
(precursors) which can be used herein, singly or in
combination, to provide oxidation hair dyes having a variety
of shades ranging from ash blonde to black; these are:
25 pyrogallol, resorcinol, p-toluenediamine, o-
phenylenediamine, m-phenylenediamine, o-aminophenol, p-
aminophenol, 4-amino-2-nitrophenol, nitro-p-
phenylenediamine, N-phenyl-p-phenylenediamine, m-
aminophenol, 2-amino-3-hydroxypyridine, N,N bis (2-
30 hydroxyethyl)p-phenylenediamine, 4-amino-2-hydroxytoluene,
1,5-dihydroxynaphthalene 2,4-diaminoanisole, hydroquinone, 4-

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amino-2-hydroxytoluene, 2-methyl resorcinol, 2-methyl-5-hydroxyaminophenol, 6-amino-3-hydroxy-toluene, 2,5-diaminotoluene, and 1-phenyl-3-methyl-pyazolone. These can be used in the molecular form or in the form of peroxide-compatible salts, as detailed above.

Applicant has also found that compositions of the present invention comprising particular oxidizing agents with particular transition metal salts or catalysts with oxidative dyes are valuable for the delivery of good high intensity colours with reduced levels of dye and peroxide. In particular applicant has now found that good hair colouring results can be achieved using the oxidizing systems of the present invention and up to about 84% less dye versus conventional hair colouring compositions. As such the compositions according to the present invention are valuable for the delivery of good initial colour and wash fastness over time in addition to having low hair damage attributes.

20

Solvents

Water is the preferred principal diluent for the compositions according to the present invention. As such, the compositions of present invention may also include one or more solvents as additional diluent materials. Generally, the solvent is selected to be miscible with water and innocuous to the skin. Solvents suitable for use herein include C₁-C₂₀ mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their

30

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ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a particularly preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol
5 monoethyl ether, and mixtures thereof.

The compositions of the invention may also include the following materials.

10

Buffering Agents

The colouring compositions of the present invention may have a pH in the range of from about 5 to about 11, more
15 preferably from about 6 to about 8, and especially from about 6 to about 7.

As herein before described the preferred colouring compositions of the present invention may contain one or
20 more buffering agents and/or hair swelling agents (HSAs) to adjust the pH to the desired level. Several different pH modifiers can be used to adjust the pH of the final composition or any constituent part thereof.

25

Thickeners

The composition containing one or more oxidative hair colouring agents of the present invention (colouring
30 compositions) may additionally include a thickener at a level of from about 0.05 % to about 20%, preferably from

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about 0.1 % to about 10%, more preferably from about 0.5% to about 5% by weight. Thickening agents suitable for use in the compositions of the invention may be selected from the group consisting of oleic acid, cetyl alcohol, oleyl
5 alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, and synthetic thickeners; and mixtures thereof.

Surfactant Materials

10 The compositions of the present invention may additionally contain a surfactant system. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to about 22 carbon atoms and can be selected from
15 the group consisting of anionic, cationic, nonionic, amphoteric, zwitterionic surfactants and mixtures thereof.

Materials used in compositions of the invention may be employed in the following ranges:

- 30 -

Hair Colouring Composition

Example 1 (which shows ranges of ingredients)	
Ingredients	% w/w
Oxidative dyes	0.01-15
Sequestrant	0.01-1
Antioxidant	0.01-3
Solvent	2.0-35
Buffering agent	0.01-10
Thickener	0.05-20
Surfactants	5.0-40
Water to	100

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Ranges of ingredients which can be included in
Hair Colouring Compositions of the invention

Example 2 (which shows ranges of ingredients)		
Ingredients		% w/w
p-Phenylenediamine	Oxidative dyes	0.0001-7
4-Amino-2-Hydroxytoluene	Oxidative dyes	0.0001-7
p-Aminophenol	Oxidative dyes	0.0001-7
2-Methylresorcinol	Oxidative dyes	0.0001-7
Phenyl-methyl-pyrazolone	Oxidative dyes	0.0001-7
N,N-bis-2-hydroxyethyl-PPD sulfate	Oxidative dyes	0.0001-7
3-Methyl-4-aminophenol	Oxidative dyes	0.0001-7
Sodium sulphite	Antioxidant	0.01-3
Sodium EDTA	Sequestrant	0.01-1
Sodium isoascorbate	Antioxidant	0.01-3
Propylene glycol	Solvent	2.0-35
Oleic acid (5 Titre)	Buffering agent	0.01-10
Isopropanol	Solvent	2.0-35
Perfume oil	Fragrance	0.1-1
Dihydroxyethyl soyamine dioleate	Surfactants	5.0-40
PEG3 Cocamine	Surfactants	5.0-40
Water		balance

5 As used here in PPD means p-phenylene-diamine.

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Ranges of ingredients which can be included in
transition metal Catalyst Compositions of the invention

1,4,7-trimethyl-1,4,7-triazacyclononane tri- \square -oxo-manganese complex	0.0001-1
Water to balance	

5

Example 3 (which shows ranges of ingredients)

Developer Formulation or composition containing water-soluble peroxygen oxidizing agent	
Chemical Name	% (w/w)
Sequestrant	0.01-1
Antioxidant	0.01-3
Solvent	2.0-35
Buffering agent	0.01-10
Thickener	0.05-20
Surfactants	5.0-40
Oxidizing agent	0.01-9
Water to balance	100

10

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Example 4 (which shows ranges of ingredients)

Catalyst Formulation (or transition metal salt or complex formulation)	
Chemical Name	% (w/w)
Catalyst	0.0001-1
Solvent	q.s.

5

Developer formulation

Oxidizing agent	0.01-9
Water to balance	to 100

10

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The following examples 5 and 6 are specific examples of a composition of the invention that was made.

5

Example 5

Ingredients	Wt %
p-Phenylenediamine	0.05
4-Amino-2-hydroxytoluene	0.0172
p-Aminophenol	0.2
2-Methylresorcinol	0.3
Phenyl-methyl-pyrazolone	0.02
N,N-bis-2-hydroxyethyl-PPD sulphate	0.001
3-methyl-4-aminophenol	0.006
Sodium sulphite	1
Sodium isoascorbate	0.15
propylene glycol	8.6
Oleic acid	8.6
Isopropanol	12.5
Perfume oil	0.5
Dihydroxyethyl soyamine dioleate	22.2
PEG3 cocamine	8
Water	q.s

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Example 6

Developer Formulation which includes the water-soluble peroxygen oxidizing agent	
Chemical Name	% (w/w)
Ceteareth-7	1
Polyquaternium 37	1
50% Hydrogen peroxide	12
85% Phosphoric acid	0.03
50% Sodium hydroxide	0.03
Water to balance	100

5

Transition metal complex which is a Manganese Catalyst Formulation	
Chemical Name	% (w/w)
Surfactant	1
1,4,7-trimethyl-1,4,7-triazacyclononane 0.01 tri- μ -oxo-manganese complex	
Water to balance	100

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Preparation of transition metal complex:

5 Add deionized water to beaker and begin mixing. Add surfactants, and thickener followed by catalyst and remaining ingredients to water.

10 Preparation of Water-soluble Peroxygen Oxidizing or Bleaching Agent Formulation which is also known as developer formulation:

 Add deionised water to beaker and begin mixing. Add
15 surfactants, thickener and buffering agents follow by oxidizing agent and remaining ingredients to water.

Preparation of dye composition- that is, the composition
20 which comprises oxidative hair colouring agents (and which may optionally be included in the compositions of the invention):

 Buffering agent, surfactants, perfume oil and solvent
25 are mixed at 55°C to obtain a homogenous solution (part 1). Deionized water is added to the beaker and mixing is continued. Antioxidants are added followed by solvent and nitrogen blanketing is begun. Dyes are added and the mixture is heated to 50-55°C and further mixed until the
30 solution is clear. The solution is cooled to 40-45°C and more water is added.

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How to use compositions of the invention

As described above, a first composition of the
5 invention comprises:

(a) a transition metal salt or complex.

As described above a second composition of the
10 invention comprises a mixture of the following two
compositions:

(a) a water-soluble peroxygen oxidizing agent;
and

15 (b) one or more oxidative hair colouring agents
selected from the group consisting of an aromatic
diamine, an aminophenol, a polyhydric phenol, a
catechol and mixtures thereof.

20 The hair to be coloured can first be made wet with
water. Then a transition metal salt or complex as described
above, can be applied to the hair. Application temperatures
may be in the range from about 15 to about 45 degrees C, or
about 15 to 40 degrees C. Then a water-soluble peroxygen
25 oxidizing agent; and one or more oxidative hair colouring
agents as described above, are thoroughly mixed together,
and soon after, this mixture is applied to the hair. Again.
application temperatures may be in the range from about 15
to about 45 degrees C or about 15 to about 40 degrees C or
30 also about 20 to about 50 degrees C. After a contact time

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of about 10 to about 45 minutes, or about 5 to about 30 minutes, the hair is thoroughly rinsed.

While the invention has been described in connection
5 with preferred embodiments, this description is not intended
to limit the invention to the particular embodiments set
forth. To the contrary, this description is intended to
cover such alternatives, modifications, and equivalents as
may be included within the spirit and scope of the invention
10 as defined by the appended claims.

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CLAIMS

1. A composition for bleaching hair which comprises a
5 first composition comprising:
 - (a) a transition metal salt or complex;
and a second composition which comprises
 - (a) a composition comprising a water-soluble peroxygen
10 oxidizing agent.
2. A composition according to claim 1, wherein said
oxidative hair colouring agent is a transition metal
15 salt and/or transition metal complex selected from
group 1B, 6B, 7B or 8B metals and an azamacrocyclic.
3. A composition according to claim 1, wherein the water-
20 soluble peroxygen oxidizing agent is selected from the
group consisting of hydrogen peroxide, sodium
perborate, sodium percarbonate, and urea peroxide
complexes.
- 25 4. A composition according to claim 2, wherein the
transition metal complex is formed from a manganese
salt and 1,4,7-trimethyl-1,4,7-triazacyclononane.

30

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10. A composition according to claim 2, wherein the transition metal salt and/or transition metal catalyst are present in a concentration ranging from about 0.0001% to about 0.2% by weight of metal equivalents relative to the total weight of composition.
11. A composition according to claim 2, wherein the transition metal salt and/or transition metal catalyst are present in a concentration ranging from about 0.001% to about 0.5% by weight of metal equivalents relative to the weight of the total composition.
12. A composition according to claim 2, wherein the transition metal salt and/or transition metal catalyst are present in a concentration ranging from about 0.001% to about 0.1% by weight of metal equivalents relative to the weight of the total composition.
13. A composition according to claim 1, which comprises one or more oxidative hair colouring agents which further comprises a buffering agent.
14. A composition according to claim 11, which has about 5 to about 11.

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5. A composition according to claim 4, wherein said manganese complex is bis(octahydro-1,4,7-trimethyl-1H-1,4,7-triazinone-N1, N4, N7)-tri-m□-oxodimanganese bis hexafluorophosphate.
- 5
6. A composition according to claim 2, wherein the weight ratio of the water-soluble peroxygen oxidizing agent to the transition metal salt and/or complex is in the range of from about 6000:1 to about 1:2.
- 10
7. A composition according to 6, wherein the weight ratio of the water-soluble peroxygen oxidizing agent to the transition metal salt and/or complex is from about 4000:1 to about 100:1.
- 15
8. A composition according to 6, wherein the weight ratio of the water-soluble peroxygen oxidizing agent to the transition metal salt and/or complex is from about 4000:1 to about 100:1.
- 20
9. A composition according to claim 7, wherein the weight ratio of the water-soluble peroxygen oxidizing agent to the transition metal complex is from about 60:1.
- 25
- 30

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15. A composition according to claim 1, which further comprises a surfactant selected from the group consisting of anionic, nonionic, cationic, zwitterionic, amphoteric surfactants and mixtures thereof.

16. A process for colouring human or animal hair which comprises applying to said hair a composition comprising :

(a) from about 0.001% to about 1.0% by weight of a transition metal salt and/or transition metal complex;

and then applying to said hair a second composition which comprises the following two compositions which are mixed just prior to said second application to the hair:

(a) a composition comprising from about 0.5% to about 20% by weight of a

water-soluble peroxygen oxidizing agent;

and

(b) a composition comprising one or more oxidative hair colouring agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol, a catechol and mixtures thereof.

wherein the composition comprises from about 5 to about 11.1% by weight of the oxidative hair colouring agents.

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17. A process for lightening and colouring very dark brown or black hair which comprises applying to said hair a composition comprising :
- (a) from about 0.001% to about 1.0% by weight of a transition metal salt and/or transition metal complex; and then applying to said hair a second composition which comprises the following two compositions which are mixed just prior to said second application to the hair:
- (a) a composition comprising from about 0.5% to about 20% by weight of a water-soluble peroxygen oxidizing agent; and
- (b) a composition comprising one or more oxidative hair colouring agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhydric phenol a catechol and mixtures thereof.
- wherein the composition comprising one or more oxidative hair colouring agents has a pH of from about 5 to about 11.

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18. A hair colouring kit comprising an individually
packaged oxidizing component, an individually packaged
component having one or more hair colouring agents, and
5 an individually packaged transition metal salt and/or
transition metal complex component wherein said
components are compositions are in accordance with
claim 1.

10

19. A composition for colouring hair which comprises a
first composition comprising:
(a) a transition metal salt or complex;
and a second composition which comprises the
15 following two compositions which are mixed just
prior to application to the hair:

(a) a composition comprising a water-soluble peroxygen
oxidizing agent; and
20 (b) a composition comprising one or more oxidative
hair colouring agents selected from the group
consisting of an aromatic diamine, an aminophenol,
a polyhedric phenol, a catechol and mixtures
thereof.

25

20. A composition for colouring hair which consists of a
first composition comprising:
(a) a transition metal salt or complex;
and a second composition which comprises the following
30 two compositions which are mixed just prior to
application to the hair:

- 45 -

(a) a composition comprising a water-soluble peroxygen oxidizing agent; and

5 (c) a composition comprising one or more oxidative hair colouring agents selected from the group consisting of an aromatic diamine, an aminophenol, a polyhedric phenol, a catechol and mixtures thereof.

10

21. A process for bleaching and/or lightening hair which comprises contacting said hair with a composition in accordance with claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/13563

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/135 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 03 011237 A (UNILEVER PLC ;LEVER HINDUSTAN LTD (IN); UNILEVER NV (NL)) 13 February 2003 (2003-02-13) the whole document ---	1-21
X	DE 198 52 972 A (HENKEL KGAA) 18 May 2000 (2000-05-18) cited in the application examples page 2, line 58 page 8, line 37 - line 54 --- -/-	1-21



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/13563

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 33435 A (BLUM HELMUT ;HENKEL KGAA (DE); MAYER BERND (DE)) 8 July 1999 (1999-07-08) cited in the application examples page 20, paragraph 3 page 20, paragraph 5 -page 21, paragraph 1 ---	1-21
X	US 5 873 910 A (HENRION JEAN-CHRISTOPHE ET AL) 23 February 1999 (1999-02-23) cited in the application examples claims 1,36 ---	1-21
X	US 5 194 416 A (JURELLER SHARON H ET AL) 16 March 1993 (1993-03-16) cited in the application examples ---	1-12,14, 15
X	EP 0 507 448 A (SQUIBB BRISTOL MYERS CO) 7 October 1992 (1992-10-07) claims; examples ---	16-18,21
X	WO 01 28508 A (FORWARD JENNIFER MARY ;PRATT DOMINIC (GB); DIAS LUIS CARLOS (GB);) 26 April 2001 (2001-04-26) cited in the application claims page 24 -page 25 -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/13563

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 03011237	A	13-02-2003	WO 03011237 A2	13-02-2003
DE 19852972	A	18-05-2000	DE 19852972 A1	18-05-2000
			AU 1161000 A	05-06-2000
			WO 0029036 A2	25-05-2000
			EP 1131042 A2	12-09-2001
			JP 2002529522 T	10-09-2002
WO 9933435	A	08-07-1999	DE 19757510 A1	24-06-1999
			AU 2161899 A	19-07-1999
			WO 9933435 A1	08-07-1999
			EP 1041955 A1	11-10-2000
			JP 2001527031 T	25-12-2001
US 5873910	A	23-02-1999	FR 2757386 A1	26-06-1998
			DE 69700325 D1	19-08-1999
			DE 69700325 T2	04-11-1999
			EP 0850635 A1	01-07-1998
			ES 2136464 T3	16-11-1999
			JP 2996636 B2	11-01-2000
			JP 10182377 A	07-07-1998
US 5194416	A	16-03-1993	AU 652867 B2	08-09-1994
			AU 2969292 A	27-05-1993
			BR 9204548 A	01-06-1993
			CA 2083658 A1	27-05-1993
			CN 1075163 A , B	11-08-1993
			DE 69216786 D1	27-02-1997
			DE 69216786 T2	15-05-1997
			EP 0544519 A2	02-06-1993
			ES 2097291 T3	01-04-1997
			JP 6121933 A	06-05-1994
			KR 9608938 B1	10-07-1996
			KR 9615159 B1	01-11-1996
			MX 9206810 A1	01-07-1993
			ZA 9209186 A	26-05-1994
EP 0507448	A	07-10-1992	US 5100436 A	31-03-1992
			AU 655234 B2	08-12-1994
			AU 1213792 A	10-09-1992
			CA 2062293 A1	08-09-1992
			DE 69211045 D1	04-07-1996
			DE 69211045 T2	02-10-1996
			EP 0507448 A2	07-10-1992
			GR 3020079 T3	31-08-1996
			JP 5124940 A	21-05-1993
			US 5316551 A	31-05-1994
WO 0128508	A	26-04-2001	AU 1215501 A	30-04-2001
			EP 1221932 A1	17-07-2002
			WO 0128508 A1	26-04-2001